

Gaseous Etching for Characterization of Structural Defects in Silicon Carbide Single Crystals

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Abstract: Single crystal SiC substrates were subjected to high temperature (1575 °C) H₂/C₃H₈ gaseous etches. The etches resulted in a variety of surface features on 4H-SiC substrates that included elongated hillocks from 10 to > 100 μm in length by a few μm in width. In some 4H- and 6H-SiC substrates, the etches resulted in a continuous coverage of macrosteps. We conclude that the morphology observed after the etching process is influenced by the local Si-C bilayer stacking sequence on the surface of off-(0001) oriented substrates. A model is presented for the formation of the hillocks, based on localized transformations of the 4H substrates during the high temperature etch process.

1. Introduction

Structural defects that occur in silicon carbide (SiC) crystals include: micropipes, line dislocations, stacking faults, and low-angle grain boundaries[1]. Processes that have been used to characterize and reveal defects in SiC include: oxidation[2], etching in molten KOH[3] and high temperature etching in gaseous mixtures of H₂/HCl[4] and H₂/C₃H₈[5]. This paper focuses on the use of H₂/C₃H₈ mixtures at high temperatures to characterize and reveal structural defects in SiC crystals.

It has been known for many years that H₂ will etch SiC at elevated temperatures resulting in gaseous hydrocarbons and elemental silicon byproducts[6]. Recently, etching in H₂ prior to SiC CVD growth has been investigated by several research groups. Burk and Rowland[7] of Northrop Grumman reported that when SiC was exposed to H₂ at high temperatures, Si droplet formation was suppressed over the temperature range 1450 to 1520 °C when C₃H₈ was present in concentrations greater than 140 ppm. There were indications that etching was taking place at a temperature of 1520 °C and C₃H₈ concentrations less than 700 ppm. The SiC research group at Linköping University (LU) has carried out SiC CVD and H₂ etching experiments and have reported that H₂ can be a useful pregrowth etchant for 4H- and 6H-SiC substrates and for revealing structural features[5]. They observed elongated hillocks on H₂ etched off-axis 4H-SiC substrates but were unable to explain the source of the hillocks.

2. Experimental

An investigation of H₂/C₃H₈ etching of SiC substrates was carried out in a cold-wall quartz reactor previously described[8]. The H₂/C₃H₈ contained 100 to 200 ppm C₃H₈ to suppress Si droplet formation. Results in this paper were obtained with etch runs carried out at 1575 °C for 30 min. The SiC substrates included mostly 4H (on-axis, 3.5° and 8° tilt) and a few 6H (on-axis and 3.5° tilt) boule-grown substrates and a few on-axis polished Lely-grown -SiC single-crystal platelets. (Polished substrates with tilt angle less than 1° are considered to be “on-axis”.) The resulting etched surfaces were characterized with Nomarski differential interference contrast microscopy (NDIC) and atomic force microscopy (AFM).

3. Results

The NASA etching results were largely consistent with those of the Northrop Grumman and LU groups. A variety of surface features were observed on SiC samples following high temperature $\text{H}_2/\text{C}_3\text{H}_8$ etching. The features and density of features varied widely over a given sample and also from sample to sample. Because of space limitations, this paper will focus on several particularly important etching results.

One important result was the observation of an unusual complex pattern of macrosteps on a single -SiC Lely-grown platelet. Prior to etching, the polished Si-face of this platelet had $50\text{ }\mu\text{m}$ wide by $30\text{ }\mu\text{m}$ deep grooves cut into its surface with a dicing saw. Some results of a 30 min $\text{H}_2/\text{C}_3\text{H}_8$ etch are shown in Figs. 1 and 2. We observed that a pattern of macrosteps covered most of the platelet and the macrostep pattern matched on opposite sides of a groove as shown in Fig. 1. Also, a repeating pattern in the macrosteps was observed in a direction perpendicular to the steps. The periodicity in the pattern was confirmed with AFM as shown in Fig. 2. The number of periods extended to at least 50 cycles. AFM measurements of terraces within the pattern (assumed to be the basal plane) yielded a tilt angle of 1° . From measurements in the direction perpendicular to the steps, the length of one period (parallel to the surface) was determined to be $5\text{ }\mu\text{m}$. From the tilt angle (1°) and the period length, we calculated the vertical repeat distance (in the crystallographic c-direction) to be 88 nm (or approximately 350 times the 0.25 nm bilayer thickness for SiC).

Another important set of etching results was obtained using boule-grown 4H and 6H substrates. Macrosteps were observed on on-axis substrates of both polytypes and on some 3.5° tilt, Si-face, 4H substrates (see Fig. 3). The macrostep heights on the 6H substrates were 1.5 nm in height. In contrast, the steps for the on-axis and off-axis 4H samples were tens of nm in height, which is much larger than the 1 nm height of the c-axis repeat distance of the 4H polytype. Similar to the LU results, elongated hillocks (herein referred to as hillocks) were also observed on 3.5° tilt, Si-face, 4H samples after $\text{H}_2/\text{C}_3\text{H}_8$ etching as shown in Fig. 4. Generally, the hillocks varied in length from $10\text{ }\mu\text{m}$ to greater than $100\text{ }\mu\text{m}$. They were usually randomly distributed, but sometimes were concentrated in the vicinity of some scratches on a substrate. Each hillock contained a single faceted face that was parallel to the basal plane. Hillocks were also observed on $\text{H}_2/\text{C}_3\text{H}_8$ -etched 8° tilt, Si-face, 4H-SiC and 3.5° tilt, C-face, 4H-SiC substrates. However, more hillocks were observed on 3.5° tilt substrates compared to 8° tilt substrates. No hillocks were observed on the few 6H substrates that

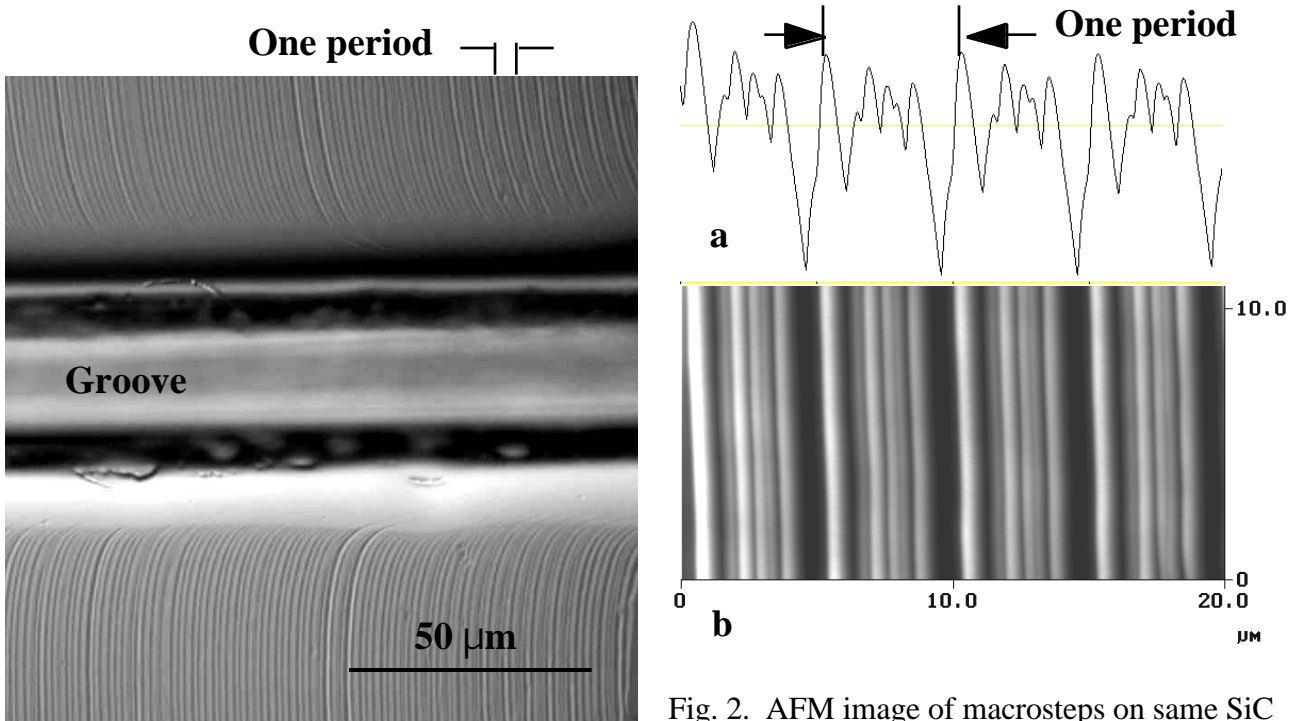


Fig. 1. NDIC image of hydrogen-etched pattern on a SiC Lely platelet. Note matched pattern on opposite sides of groove.

Fig. 2. AFM image of macrosteps on same SiC Lely platelet as in Fig. 1. (a) Cross-sectional profile, (b) Plan view: dark to light 25 nm vertical.

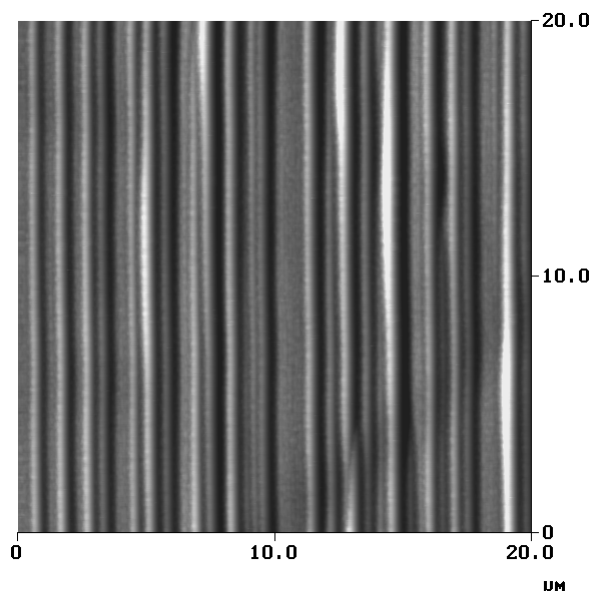


Fig. 3. AFM image (plan view) of macrosteps on an etched 3.5° tilt, Si-face, 4H-SiC substrate. Dark to light: 30 nm vertical.

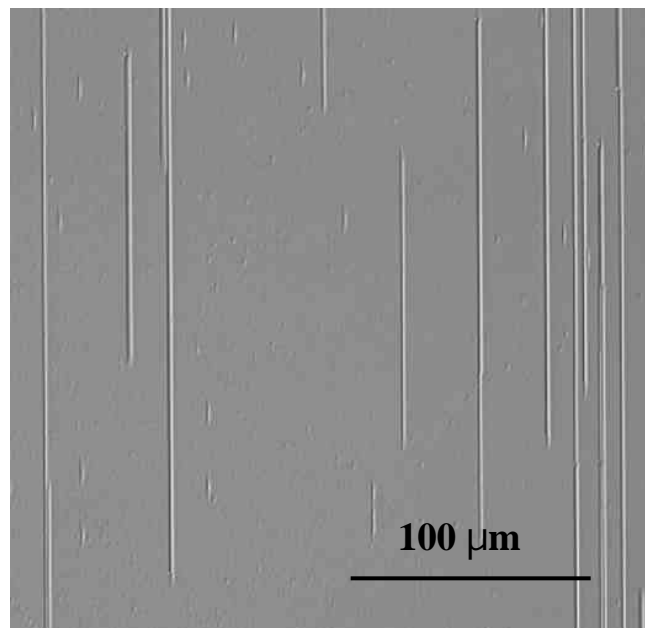


Fig. 4. NDIC image of elongated hillocks on an etched 3.5° tilt, Si-face, 4H-SiC substrate.

were studied. In all observed cases, the macrosteps and hillocks were parallel to the naturally occurring atomic steps that were produced by the off-axis polishing of the samples.

4. Discussion

The following is a model we propose to explain the above observations, starting with the Lely platelet results. We believe that the complex macrostep pattern observed on the “etched” Lely platelet was much more likely caused by a feature of the bulk structure, rather than by some surface phenomenon. This belief is based on the observations of (1) matching macrostep patterns on opposite sides of the grooves, and (2) the repeating nature of the macrostep pattern. We also believe that the periodic macrostep pattern indicates that the Lely crystal contains a “super” polytypic stacking sequence (e.g. a 350H? structure). We further conclude that, under the conditions of the H_2/C_3H_8 etch (either the high temperature aspect of the etch or a combination of the high temperature and the etching), the surface morphology is modified during the “etch” in a manner that reflects the local variations in the bilayer stacking sequence.

There are reasons to believe that SiC etch rates can be a function of the local environment of the bilayers. Each bilayer within a SiC stacking sequence is considered to be in either a locally hexagonal or cubic environment[9]. The etch rate of a cubic bilayer may also be a function of its local orientation. The reasons are the following. The cubic and hexagonal SiC polytypes oxidize at different rates [2]. Also, the step flow growth rate of a cubic bilayer is a function of the crystallographic orientation parallel to the basal plane[10]. Based on all of the above considerations, we conclude that an off-axis SiC surface could chemically etch in a manner that reflects the pattern of cubic and hexagonal bilayers in the surface.

We also recall observations that solid-state phase transformations in 2H-SiC were greatly enhanced by defects caused by polishing[11]. Phase transformations took place in polishing-damaged 2H crystals at temperatures as low as 400 °C. The 2H transformations were toward a more cubic (less hexagonal) structure. Since the percent hexagonality[9] of the 4H structure (50% hexagonal) is between that of 2H (100% hexagonal) and 6H (33% hexagonal), we speculate that the 4H structure ranks somewhere between 2H and 6H in stability. In another paper in these proceedings[12], evidence is presented that at least some triangular 3C SiC inclusions observed in 4H-SiC epitaxial films were formed by a solid state phase transformation from the 4H matrix. Finally, Pirouze [13] proposed a kinetic mechanism for the 4H to 3C phase transformation in the presence of dislocations. These ideas suggest that 4H may be susceptible to solid state transformation under certain conditions.

We now apply these interpretations and ideas to the observation of the hillocks and the macrosteps in the $\text{H}_2/\text{C}_3\text{H}_8$ etched 4H substrates. We speculate that at least some of the hillocks and/or macrosteps are caused by localized transformations under the conditions of the $\text{H}_2/\text{C}_3\text{H}_8$ etch and that that residual subsurface polishing damage acts to enable the transformations. Some macrosteps may have their origin in basal plane stacking faults that existed in the bulk crystal. The single large macrostep at each hillock suggests a local change in the stacking sequence that extends for some distance along the basal plane. It remains to be determined whether the morphological changes are due to the high temperature only, or to a combination of temperature and chemical etching. The increased density of hillocks in the vicinity of some scratches is consistent with the increased density of subsurface damage along scratches. Further, macrosteps may be created by the coalescence of a large density of hillocks where the subsurface damage is sufficiently dense.

5. Concluding Remarks

The results of this work have demonstrated that H_2 etching can be useful in characterizing and revealing defects in SiC substrates. More important, the results indicate that heating 4H-SiC substrates in a H_2 environment may alter the surface structure. The presence of such structural changes could have a detrimental effect on subsequently fabricated devices. If the proposed model is confirmed by additional work, future 4H device fabrication processes, including epitaxial growth, will have to be modified. If only heating is sufficient to cause transformation, annealing of 4H-SiC to high temperatures in inert atmospheres (e.g. after ion implantation) will also be affected. Hopefully, if the 4H-SiC surfaces are properly prepared without subsurface damage (e.g. through the use of chemomechanical polishing), the transformation effects may be prevented.

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